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RESEARCH ARTICLE

Surface ozone in the Colorado northern Front Range and the influence of oil and gas development during FRAPPE/DISCOVER-AQ in summer 2014

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High mixing ratios of ozone (O_3) in the northern Front Range (NFR) of Colorado are not limited to the urban Denver area but were also observed in rural areas where oil and gas activity is the primary source of O_3 precursors. On individual days, oil and gas O_3 precursors can contribute in excess of 30 ppb to O_3 growth and can lead to exceedances of the EPA O_3 National Ambient Air Quality Standard. Data used in this study were gathered from continuous surface O_3 monitors for June–August 2013–2015 as well as additional flask measurements and mobile laboratories that were part of the FRAPPE/DISCOVER-AQ field campaign of July–August 2014. Overall observed O_3 levels during the summer of 2014 were lower than in 2013, likely due to cooler and damper weather than an average summer. This study determined the median hourly surface O_3 mixing ratio in the NFR on summer days with limited photochemical production to be approximately 45–55 ppb. Mobile laboratory and flask data collected on three days provide representative case studies of different O_3 formation environments in and around Greeley, Colorado. Observations of several gases (including methane, ethane, CO, nitrous oxide) along with O_3 are used to identify sources of O_3 precursor emissions. A July 23 survey demonstrated low O_3 (45–60 ppb) while August 3 and August 13 surveys recorded O_3 levels of 75–80 ppb or more. August 3 exemplifies influence of moderate urban and high oil and gas O_3 precursor emissions. August 13 demonstrates high oil and gas emissions, low agricultural emissions, and CO measurements that were well correlated with ethane from oil and gas, suggesting an oil and gas related activity as a NOx and O_3 precursor source. Low isoprene levels indicated that they were not a significant contributor to O_3 precursors measured during the case studies.

Keywords: surface ozone; oil and gas; FRAPPE/DISCOVER-AQ; Colorado northern Front Range

Introduction

The Front Range of Colorado contains the region lying east of the foothills of the Rocky Mountains, from north of Colorado Springs to north of Fort Collins, and east encompassing the Denver-Julesburg (D-J) Oil and Gas Basin. Larger municipalities in the Front Range include Denver, Boulder, Longmont, Fort Collins, and Greeley. The D-J Basin is the site of major oil and gas developments as well as agriculture (crops and cattle). Since 2007, the Front Range has been classified by the U.S. EPA as a non-attainment area for ozone (O_3) due to its summertime exceedances of the National Ambient Air Quality Standard (NAAQS) for O_3. The EPA regulates ground-level O_3 by specifying that the fourth-highest daily maximum 8-hour time averaged mixing ratio, averaged across three consecutive years, may not exceed 75 ppb (U.S. EPA, 2013a). In 2015 the EPA lowered the NAAQS standard to 70 ppb which is likely to be exceeded by the Denver and northern Front Range (NFR) when the new nonattainment designation is released at the end of 2017 (CDPHE, 2015). For this study, unless stated otherwise, the NAAQS refers to the 75 ppb standard that was in place July–August 2014 during the FRAPPE/DISCOVER-AQ field campaign.

In 2014 Colorado was ranked the 5th highest state in the US for total number of oil and natural gas wells with 7,771 oil and 46,876 natural gas wells (EIA, 2015). Weld County, located between Denver and Greeley, is the most densely drilled region of the D-J Basin; from 2010 to 2014 annual oil production increased from 21 to 81 million barrels and annual gas production increased from

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219 to 392 billion cubic feet in Weld County (COGCC, 2014a). Volatile organic compounds (VOCs) and nitrogen oxides (NOx) emitted by oil and gas extraction activities are surface O_3 precursors. According to a study by Pétron et al. (2014) based on aircraft measurements in May 2012, the Colorado state inventory for total VOCs emitted by oil and gas activities was at least a factor of two below actual measured emissions. The 2014 EPA National Emissions Inventory estimated that in Weld County, oil and gas contributes to 80% of total point source VOC emissions (U.S. EPA, 2014). Studies by Gilman et al. (2013) and Eisele et al. (2009) also indicate that oil and gas development is the primary VOC source by mass in Boulder and Weld counties and potentially a key contributor to summertime O_3 exceedances. During the spring and summer of 2015, oil and gas related VOCs measured at the NOAA Boulder Atmospheric Observatory (BAO) Tower (located 20 miles north of Denver) accounted for 40–60% of VOC reactivity with hydroxyl radicals (Abeleira et al., 2017). Swarthout et al. (2013) measured VOC distributions at BAO tower during winter 2011 and concluded that the strongest source of VOCs was northeast of BAO, where the alkane pattern matched the signature of natural gas from the Wattenberg oil and gas field. Urban combustion was identified as the major VOC source south of BAO. The Front Range does have stringent air emissions regulations for most oil and gas operations; in 2014 the State passed rules mandating detection and fixing of methane leaks and a 95% capture of well pad emissions, specifically with the goal of controlling O_3 production due to oil and gas VOCs (Code of Colorado Regulations, 2016). Enforcement of some of these regulations began May 2014, but during the measurement campaign when this study took place they might not have been fully implemented. It is possible that not all emission mitigation has been as effective as required and continuous monitoring of emissions from oil and gas related activities is necessary to evaluate compliance (U.S. EPA, 2015).

Methane, a major trace gas in fugitive emissions from oil and gas operations, only reacts to form O_3 on longer time scales and thus is not a precursor at the regional scale (Fiore et al., 2008). But, methane is commonly used as a marker of non-methane hydrocarbon (NMHC) O_3 precursor VOCs emitted from oil and gas operations. Ethane is an example of a NMHC O_3 precursor that is co-emitted with methane; elevated methane and ethane indicates the presence of oil and gas emissions (Helmig et al., 2016). Due to the relatively long lifetime of ethane (~2 months) it is not a major contributor to O_3 production on short time scales, but it is co-emitted with other NMHCs that react faster in the atmosphere to form O_3 (Helmig et al., 2016). Background methane levels measured by aircraft in the planetary boundary layer in the NFR were 1.846–1.876 ppm in May 2012 (Pétron et al., 2014) and the regional annual average background ethane mixing ratio reported by Thompson et al. (2014) was 1.29 ppb. Other major sources of methane in the Front Range include beef and dairy production, large landfills, and wastewater treatment plants (Pétron et al., 2014). Concentrated animal feeding operations (CAFOs), including cattle feedlots, are known sources of methane, nitrous oxide, and ammonia from manure waste management and enteric fermentation in cattle. Landfill emissions are constituted of approximately 50% methane, 45% carbon dioxide, and the balance a mixture of trace gases including small amounts of NMHCs (Czepiel et al., 1996). Both animal operations and landfills do not emit ethane or light alkanes. There are a substantial number of wastewater treatment plants in the Front Range that potentially emit carbon dioxide, methane, and nitrous oxide (Gupta and Singh, 2012). CAFOs, landfills, and wastewater treatment plants are relatively small sources of methane in Weld County compared to the 75% of methane emissions attributed to oil and gas operations by a study in May 2012 (Pétron et al., 2014).

Inventory estimates for Colorado in 2014 attributed 40% of total NOx emissions to vehicles while petroleum and related industries were estimated to contribute 14% of NOx emissions (U.S. EPA, 2011; U.S. EPA, 2014). According to the National Emissions Inventory (NEI), statewide absolute NOx emissions from 2011 to 2014 decreased from 337,093 to 305,556 tons/yr. However NOx emissions in Weld County increased from 32,696 to 33,275 tons/yr during that same time period, mostly due to large increases in NOx from petroleum and related industries. The concurrent changes in VOC and NOx emissions could have large impacts on summertime O_3 production in and downwind of the NFR; however, the relative contributions of these precursor sources to O_3 levels throughout the region have not been well quantified. O_3 production can occur in either NOx-limited or VOC-limited regimes. Highly trafficked urban areas that are saturated with NOx emissions from vehicles are often more limited in terms of O_3 growth by VOC emissions, whereas more rural areas with high biogenic VOC emissions and low NOx levels are typically NOx-sensitive. The Front Range has low biogenic VOC emissions compared to other oil and gas-producing regions in the U.S. such as eastern Texas and Pennsylvania; consequently O_3 production may be more sensitive to increases in VOCs from the local oil and gas operations emissions (McDuffie et al., 2016). Biogenic VOC levels are highly dependent on environmental conditions such as drought stress, and may contribute more significantly to overall VOC reactivity in the Front Range depending on the year (Abeleira et al., 2017). While rural areas are generally more NOx sensitive, there are circumstances where less urbanized areas can be VOC-limited. For example, Front Range inversions can trap Denver NOx emissions in the Platte River Valley (north of Denver) and cause the region to be more VOC-limited (Reddy, 2008).

Several studies have analyzed the O_3 production resulting from oil and gas emissions in the Uintah Basin, Utah (Edwards et al., 2014; Schnell et al., 2016; Oltmans et al., 2016) as well as in the Upper Green River Basin, Wyoming (Schnell et al., 2009; Oltmans et al., 2014; Rappenglück et al., 2014; Field et al., 2015). However, the Colorado Front Range contains more complex land use patterns and population distributions than those areas. McDuffie et al. (2016) used an observationally constrained chemical box model to study the contributions of oil and gas VOCs to photochemical surface O_3 production at the BAO Tower

for two summer periods (July–August 2012 and 2014). They found that although on average, oil and gas VOCs contribute 2.9 ppb to daily maximum photochemical O_3 at BAO; the contribution could be as high as 6 ppb on days with more sunlight and higher photolysis rates. Their conclusions identified a need for more spatially distributed studies in order to characterize the various sensitivities of O_3 production in the Front Range, as well as to better understand the interactions of the complex mix of emission sources in the region. Another study used surface ozone and wind observations at the BAO Tower and a South Boulder monitoring site from 2009–2012 to identify potential transport of elevated ozone in the Front Range (Evans and Helmig, 2016). They found that 65% of one-hour averaged elevated ozone levels were associated with transport from areas of oil and gas operations, while only 9% of elevated ozone was correlated with winds from the Denver urban corridor. Both of these studies reported average contributions from oil and gas to O_3 production, a useful metric to help quantify the impact of oil and gas on surface O_3, but not the only aspect to consider when evaluating the relevance of the issue to regulatory NAAQS compliance. Exceedances of EPA standards are based on the four highest 8-hour maxima throughout the year, not overall enhancement averaged over multiple days; therefore, it is important to study the impact oil and gas emissions can have on individual high O_3 daily episodes to support regulatory efforts to comply with the NAAQS.

A major goal of this study is to examine individual high O_3 episodes and evaluate the contributions of oil and gas precursors to O_3 production using three case studies. The paper first provides an overview of surface O_3 distribution in the NFR, specifically during the summer of 2014 when the FRAPPE/DISCOVER-AQ campaign took place. The overview includes a discussion of underlying O_3 mixing ratios in the region, O_3 daytime growth rates, surface wind patterns, a comparison of 2014 to other years, and a summary of O_3 spatial variation at the surface sites in the NFR. The second half of the paper focuses on three case study dates during the FRAPPE/DISCOVER-AQ field campaign when there were mobile laboratory drives in addition to a variety of other surface measurements. The purpose of the case studies is to show different O_3 formation conditions in a remote area in the northeast corner of the Denver-Julesburg-Wattenberg oil and gas field and to evaluate the influence of oil and gas emissions on specific high O_3 days. Analysis of these case studies is a key step used in determining the potential sources of O_3 precursors in order to evaluate the relative contributions of emissions sectors in the NFR to O_3 growth.

Methods

Observations utilized in this study were gathered from fixed surface O_3 monitoring sites, mobile laboratories, discrete air samples in flasks, and meteorological stations. An overview of the monitoring site locations as well as the different pollutant sources in the study region is shown in **Figure 1**. Although the Front Range includes the Denver Metropolitan area, this investigation was focused on the NFR from Boulder to Fort Collins and east.

Fixed surface O_3 monitoring sites included three operated by the Colorado Department of Public Health

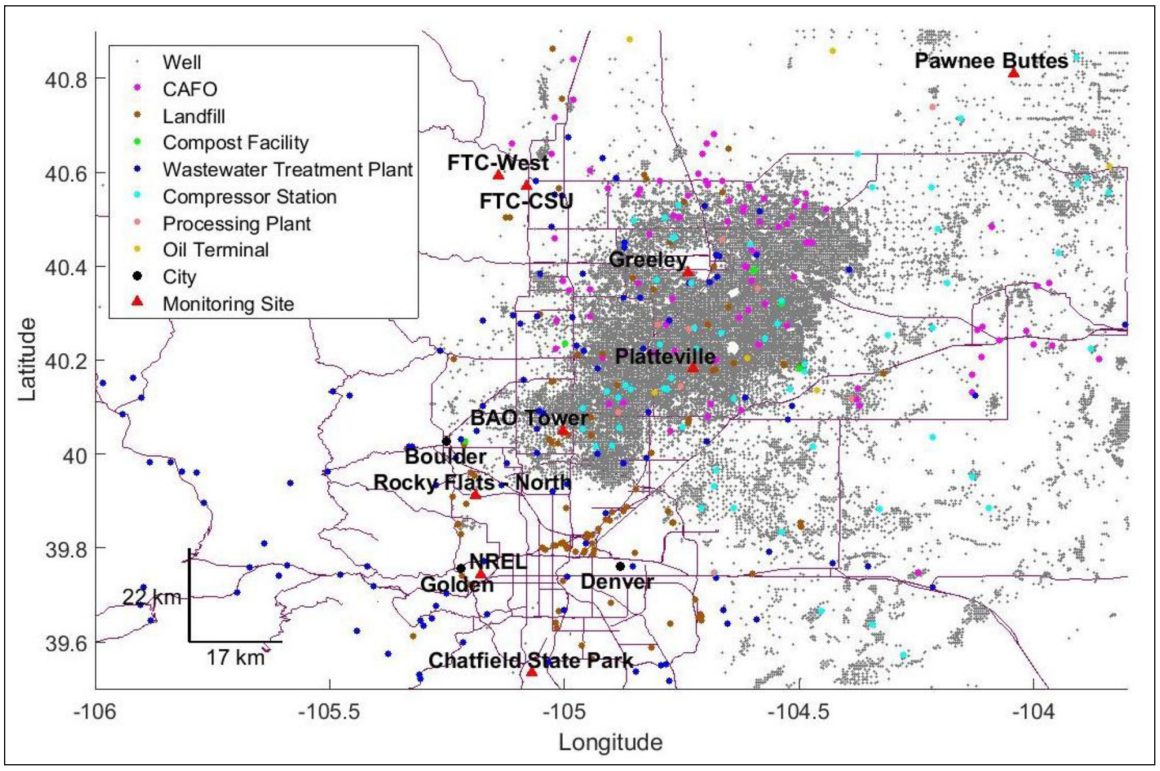

Figure 1: Map of Front Range with monitoring sites and potential emission sources. Map of the Front Range showing monitoring sites and methane and potential O_3 precursor sources (color coded dots) (COGCC, 2014b, D Wells, CDPHE, personal communication, July 2014). DOI: https://doi.org/10.1525/elementa.254.f1

and Environment (CDPHE), the BAO tall tower in east Erie operated by the National Oceanic and Atmospheric Administration Global Monitoring Division (NOAA/GMD), a site in Pawnee National Grassland operated by the US Forest Service, Rocky Mountain Research Station, a site near Platteville operated by the NOAA Chemical Sciences Division (CSD), and a site near Platteville operated by NASA/Goddard and the Pennsylvania State University. Two of the CDPHE sites are located in Fort Collins and the third is operated at the Weld County Tower site in Greeley. All data from the fixed sites were converted to hourly averages for this study and raw data are available in the data archive on the NASA DISCOVER-AQ website (NASA, 2015). Hourly averaged O_3 data for June, July, and August of 2013 and 2014 at Platteville were obtained from the NOAA CSD who operated a surface O_3 monitoring site from 2011 until August 29, 2014 (NOAA CSD, 2014). Reference instruments at the three CDPHE sites and the Pawnee Buttes site were calibrated in accordance with U.S. EPA protocols (U.S. EPA, 2013b). Surface O_3 observations from the NOAA/GMD sites have undergone thorough evaluation and extensive quality control following calibration procedures available through the World Meteorological Organization (Galbally et al., 2013). A list of the seven surface O_3 sites is provided in **Table 1**.

The mobile laboratory data were provided by the Aerodyne group, which used a 2B Tech. 205 to measure O_3 (operated in accordance with federal method EQOA-0410-190), a LICOR to measure CO_2, and Aerodyne tunable infrared laser direct absorption spectrometer based instruments (TILDAS) to measure methane, ethane, ammonia, nitrous oxide, and carbon monoxide (CO) (Herndon et al., 2005; McManus et al., 2015; Yacovitch et al., 2014). Sensitivity limits, noise statistics, calibration procedures, and quality assurance for the Aerodyne TILDAS are described in detail by Herndon et al. (2005), McManus et al. (2015), Yacovitch et al. (2014), and Yacovitch and Herndon (2014). Mobile laboratory O_3 measurements when in close proximity (<1 km) to the Greeley monitoring site are in good agreement (on average the differences are <3 ppb over a wide range of O_3 mixing ratios) (see Supplemental Material Figures S1–S3). The sampling frequency of O_3 was every 2 seconds and all other gases on the mobile laboratory platform were measured every second. Two 2D anemometers were mounted on the mobile laboratory (3.2 m above the ground and 1.6 m in front of the roof line) to measure wind speed and wind direction: an AIRMar 200WX (with built in GPS, 1 Hz logging frequency) that internally compensated for vehicle movement, and a RM Young (4 Hz logging frequency) coupled with a Hemisphere V103 GPS compass. True wind measurements from this tandem of instruments were determined using an algorithm (~3% uncertainty for one-minute averaged data while moving), and all meteorological data were filtered to exclude wind speeds below 2.5 m/s in accordance with methods used by Pétron et al. (2012). For use in this study, all mobile laboratory data were time-averaged to a one-minute resolution. The mobile laboratory data were filtered for wind direction and vehicle speed to exclude data that may have been impacted by its own vehicular emissions; for all vehicle velocities below 7 mph any measurements from the rear direction were removed.

Discrete halocarbon/hydrocarbon grab samples were collected by another mobile laboratory operated by a University of California Irvine (UCI) research group using stainless steel evacuated flasks. The samples were analyzed with both GC and GC/MS at UCI (Colman et al., 2001). Species of interest to this study included ethane, propane, n-butane, n-pentane, benzene, and isoprene. Air samples were taken at a variety of locations throughout the Front Range, detailed specifically in the case study section below.

Table 1: Summary of fixed surface O_3 monitoring sites. DOI: https://doi.org/10.1525/elementa.254.t1

Site Name	Organization	Latitude (decimal degrees)	Longitude (decimal degrees)	Site Altitude (masl)	O_3 Measurement Inlet Height (magl)	O_3 Analyzer (all instruments UV Absorption Analyzers)	Wind Data Available?
BAO Tower	NOAA/GMD	40.050°	−105.004°	1584	6	Thermo-Scientific Model 49C	Yes
Pawnee Buttes	US Forest Service, Rocky Mountain Research Station	40.810°	−104.043°	1658	2	2B Technologies Model 202	No
Fort Collins – CSU	CDPHE	40.571°	−105.080°	1530	3	Teledyne API E400	Yes
Fort Collins – West	CDPHE	40.593°	−105.141°	1571	3	Teledyne API E400	No
Greeley	CDPHE	40.386°	−104.737°	1483	3	Teledyne API E400	Yes
Platteville	NASA/Goddard & Penn State University	40.182°	−104.727°	1523	4	Thermo-Scientific Model 49C	Yes
Platteville	NOAA/CSD	40.183°	−104.726°	1523	10	Thermo-Scientific Model 49C	No

Air mass backward trajectory analyses were completed using NOAA's HYSPLIT atmospheric transport and dispersion modeling system (Stein et. al., 2015; Rolph et al., 2017). Five-hour back trajectories were calculated for each of the three case study dates at a height of 300 m agl using the North American Model (NAM) 12 km meteorological reanalysis. Ending times were selected to coincide with the timing of the mobile laboratory routes, and the five-hour length was chosen to encompass the period of potential photochemical O_3 production. Ending locations of the trajectories were set to correspond in position to the location of the mobile laboratory at the time of the trajectory.

Results and discussion

Overview of surface O_3 in the NFR

O_3 growth

Before investigating the relative contributions of different pollution sources to higher O_3 production, it is important to estimate the median summertime level of O_3 without significant photochemical production. For this purpose, **Figure 2** is used to estimate the underlying O_3 distribution on days when the O_3 mixing ratios are minimally impacted by boundary layer photochemical production (peak less than 60 ppb). This value is representative of the O_3 mixing ratio due to boundary layer mixing with the free troposphere, limited regional production, and average levels of titration of O_3 with NO. Days with peak hourly O_3 values <60 ppb are ~35% (28–44%, depending on the site) of all summer days in 2013, 2014, and 2015 (June–August) at the Front Range locations. The plot shows there is an increase in O_3 from approximately 7:00 to 13:00 (all times in this study are reported in Mountain Daylight Time (MDT)) and the O_3 mixing ratio levels out around 45–55 ppb in the afternoon. The morning growth rate falls in the range ~2.2–7.2 ppb/hr at the Front Range sites on lower O_3 days.

Median summertime limited photochemical production O_3 mixing ratios were estimated by examining values of O_3 at Pawnee Buttes on days when the peak was less than 60 ppb (116 of 276 days). The Pawnee Buttes site was selected because it is representative of a less polluted area; normally it experiences lower daytime O_3 growth rates and less O_3 depletion at night from reaction with NO compared to the other surface monitoring sites. As **Figure 2** shows, the median daytime maximum O_3 mixing ratio at Pawnee Buttes was 52 ppb, with 25th and 75th percentile values of 48 and 55 ppb, respectively. Based on these estimates, the O_3 mixing ratio on days with limited photochemical production in the NFR region is determined to be within the range of approximately 45–55 ppb. O_3 levels measured above this value are likely due to more significant photochemical production and can be enhanced by pollution sources such as oil and gas activities and urban emissions.

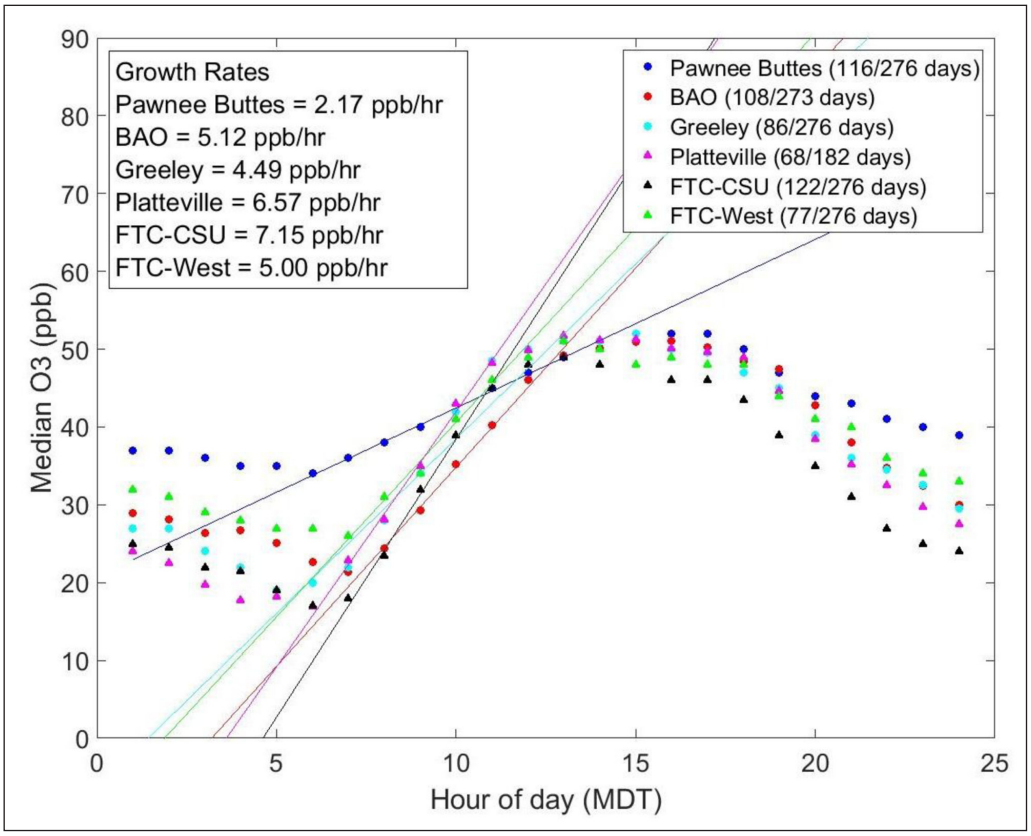

Figure 2: Median O_3 growth rates at six surface sites on low peak O_3 days. Median O_3 binned by hour of day for all days with peak mixing ratio less than 60 ppb including June, July, and August of 2013, 2014, and 2015 (Platteville only 2013 and 2014). The fraction of total days included are shown in the legend for each site. Growth rates estimated using linear fit lines (solid lines color coded by site) for period of constant O_3 increase at each site. DOI: https://doi.org/10.1525/elementa.254.f2

On days of high O_3, the morning O_3 growth continues into the afternoon and peaks around 15:00. This phenomenon is shown in **Figure 3**, which is similar to **Figure 2** but contains only dates where the peak hourly mean O_3 was ≥75 ppb. The growth rates are higher than the low-O_3 days due to the simultaneous occurrence of boundary layer mixing and photochemical production; the growth also continues later into the day when photochemical production dominates the O_3 growth. Growth rates were ~4.2–11 ppb per hour; about twice those under conditions represented in **Figure 2**. The growth rate at BAO was lower than at Platteville or Greeley by ~3 ppb/hr, which is significant as previous studies on VOCs from oil and gas activities and O_3 production in the Front Range have based their findings on data from BAO Tower (Gilman et al., Swarthout et al., 2013; Evans and Helmig, 2016; McDuffie et al., 2016; Abeleira et al., 2017). Based on benzene measurements by Halliday et al. (2016), located more centrally in the gas field in Platteville, other areas in the Front Range are more impacted by oil and gas emissions than BAO. These results, in addition to **Figure 3**, show that O_3 production at BAO is somewhat moderate compared to locations further towards the center of the D-J Basin such as Platteville. Previous studies based on data collected at BAO have likely not captured the maximum influence of oil and gas emissions on O_3 production. In **Figure 3**, days with peak hourly values ≥75 ppb represent ~15% (10–22%) of all days through the summer, except at the minimally polluted Pawnee Buttes site where only 4% of days had values ≥75 ppb. The summer months of 2014 had fewer days than 2013 or 2015 with peak hourly values ≥75 ppb at the surface sites included in **Figure 3**, indicating that 2014 was lower than average summers in terms of high O_3 episodes. These high O_3 days are of particular interest since they represent potential exceedances of the NAAQS for O_3. High O_3 episodes may not follow the average production patterns reported by studies such as McDuffie et al. (2016), yet they are important when considering health effects and regulatory exceedances.

Wind direction and surface O_3

The local meteorology of the region is strongly influenced by its complex terrain setting in the lee of the Rocky Mountains. Diurnal, thermally driven flows are a common meteorological feature of the surface air in the Front Range, especially during the months of April through September (Losleben et al., 2000). Upslope flow is caused by rapid surface heating on eastward facing foothill and mountain slopes during the morning that leads to the warm air near the surface rising and forming winds from the east with a slight southerly component (Toth and Johnson, 1985; Watson et al., 1998). In the late afternoon, the pattern is

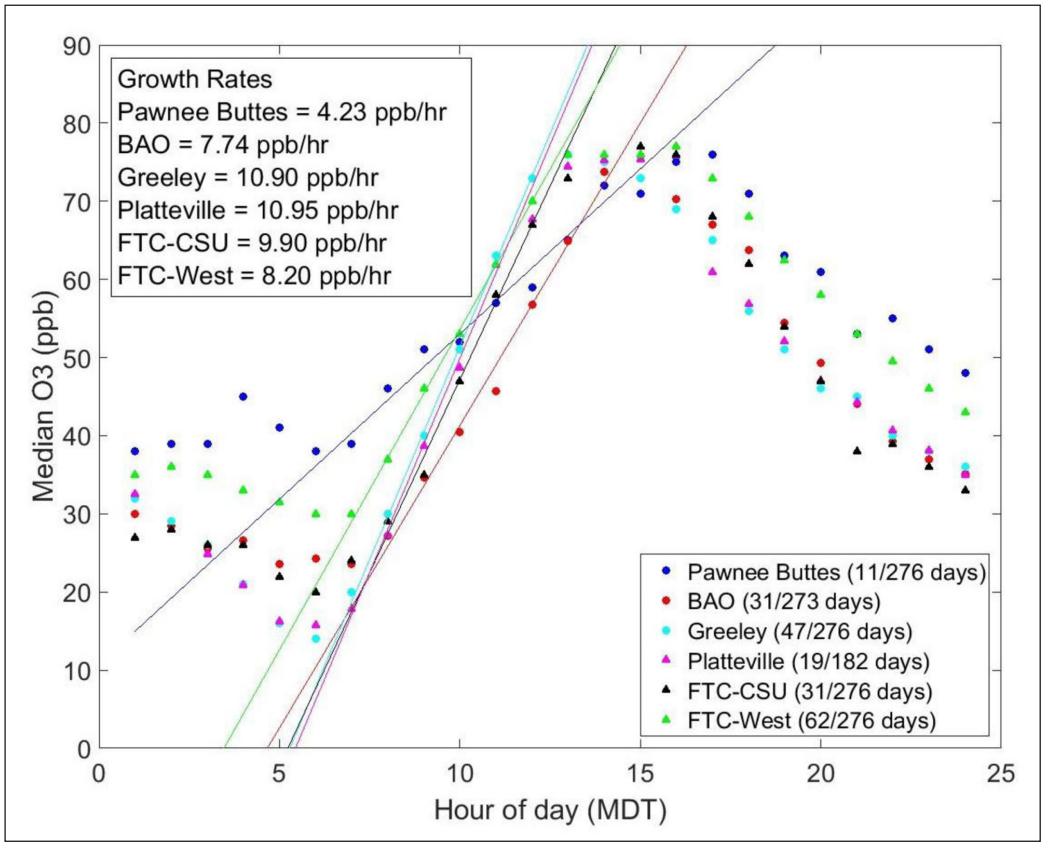

Figure 3: Median O_3 growth rates at six surface sites on high peak O_3 days. Median O_3 binned by hour of day for all days with peak mixing ratio greater than 75 ppb including June, July, and August of 2013, 2014, and 2015 (Platteville only 2013 and 2014). The fraction of total days included are shown in the legend for each site. Growth rates estimated using linear fit lines (solid lines color coded by site) for period of constant O_3 increase at each site. DOI: https://doi.org/10.1525/elementa.254.f3

reversed and the winds come from the west and go down the mountain slopes. Upslope flow earlier in the daytime has the potential to transport air pollutants out of the D-J Basin and throughout the Front Range; downslope flow overnight has the potential to transport pollutants back (Halliday et al., 2016).

The air circulation patterns throughout the Front Range influence the transport of O_3 precursors and consequently impact the O_3 measured at the monitoring stations (Evans and Helmig, 2016). The plots shown in **Figure 4** are polar histograms that display the O_3 mixing ratios based on wind directions at Fort Collins – CSU and Greeley from 5:00–10:00 (a, c) and 10:00–15:00 (b, d) including all days from July 16 to August 10, 2014 – the period of FRAPPE/Discover-AQ. The frequency of wind direction measurements is represented by the bar length and the O_3 mole fractions are differentiated by colors. The wind direction is dominated by the upslope-downslope trends, with winds prevailing from the north and west from 5:00–10:00 and from the southeast and east from 10:00–15:00. At Fort Collins – CSU from 10:00–15:00, the winds display a clear pattern and originate in the southeast. Relative to the monitoring station, the winds are coming predominantly from the general direction of Platteville and the surrounding areas with dense oil, gas, and agricultural activities. Longer range transport of emissions from Denver, lying to the south-southeast of the monitoring station, and sources within Fort Collins, a city of over 150,000 inhabitants, were potential sources of urban O_3 precursors. Greeley's more central location in the Wattenberg oil and gas field and dominant easterly winds bring a mixture of O_3 precursors from urban, oil and gas, and agriculture during the time of peak photochemical O_3 production.

Summer 2014 surface O_3

O_3 measurements in Colorado have fluctuated above and below the 2008 NAAQS standard of 75 ppb, with an overall increasing trend since 2009, although 2014 and 2015 were slightly lower than previous years (CDPHE, 2016). The CDPHE Air Pollution Control Division states that the recent oil and gas development in Colorado, in addition to overall economic growth since 2010, may be a contributor to the measured O_3 growth (CDPHE, 2016). The weather during the FRAPPE/DISCOVER-AQ study period of July and August, 2014 was relatively cool and damp, with high thunderstorm activity that can inhibit OH radical generation and O_3 production even in the presence of adequate precursors for O_3 production (McDuffie et al., 2016). July 2014 was the 11th wettest July since 1872 and August 2014 was the 19th wettest August (NWS, 2015). **Table 2** summarizes the O_3 monitoring for 2013, 2014, and 2015 in metrics used

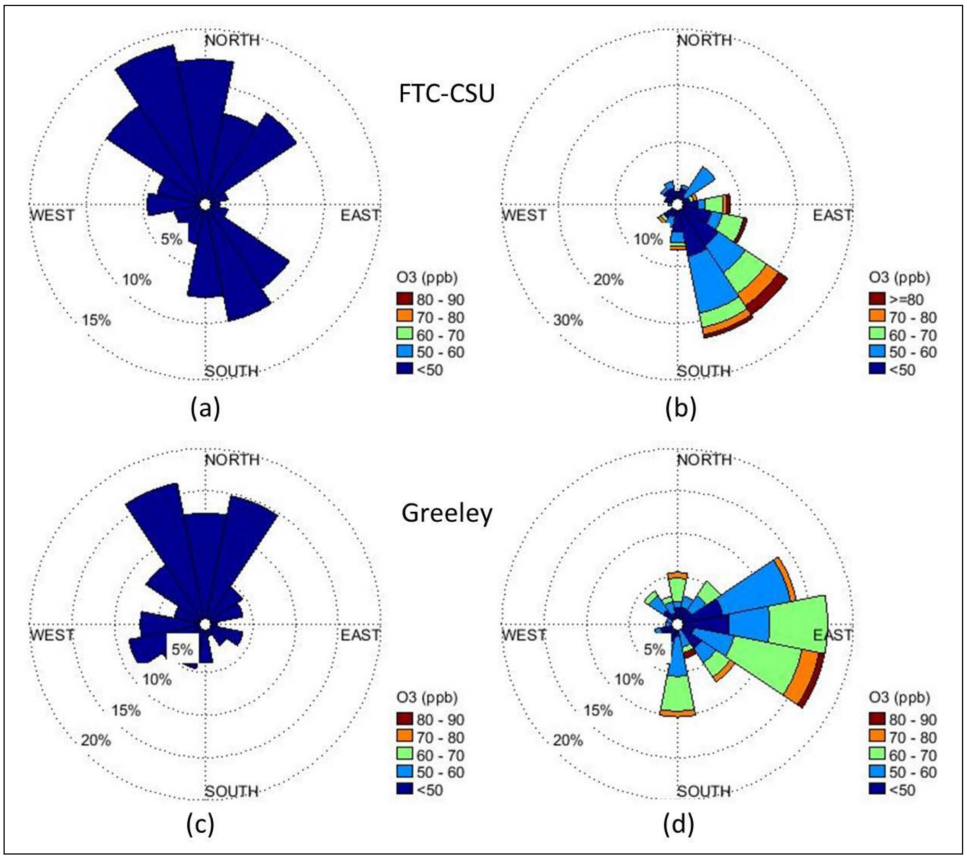

Figure 4: FTC-CSU and Greeley polar O_3 histograms. Polar histograms with O_3 mole fractions based on wind direction at FTC-CSU from 5:00–10:00 **(a)** and 10:00–15:00 **(b)** and at Greeley from 5:00–10:00 **(c)** and 10:00–15:00 **(d)** for July 15 to August 10, 2014. O_3 mixing ratios (in ppb) are indicated by color and the percentages represent the frequency of wind coming from a particular direction. DOI: https://doi.org/10.1525/elementa.254.f4

Table 2: Maximum O_3 mixing ratios observed at sites in the Denver metro area and NFR region in 2013, 2014, and 2015 (reported by CDPHE). DOI: https://doi.org/10.1525/elementa.254.t2

Site Name	1st 8-Hour Maximum (ppb)			4th 8-Hour Maximum (ppb)		
	2013	2014	2015	2013	2014	2015
Welby	82	73	75	77	67	69
Aurora – East	81	77	81	73	67	68
South Boulder Creek	86	75	79	79	70	74
CAMP	74	68	77	67	61	67
La Casa	80	69	80	71	66	71
Chatfield State Park	86	77	93	83	74	81
Welch	84	70	85	80	66	75
Rocky Flats – N	93	82	81	85	77	77
NREL	90	79	91	84	76	81
Aspen Park	80	70	74	77	65	70
Fort Collins – West[a]	91	82	80	82	74	75
Fort Collins – Mason (CSU)[a]	83	74	76	74	72	69
Greeley – Tower[a]	80	78	77	73	70	73

[a]Sites included in this study.

to classify NAAQS exceedances. 2014 showed lower 1st 8-hour maximums and 4th 8-hour maximums than 2013 and 2015 for all monitoring sites, demonstrating the impact the cool and wet conditions of summer 2014 had on photochemical O_3 production.

Based on the 2014 4th maximum 8-hour average, the sites with the highest O_3 were Rocky Flats – North, NREL, Chatfield State Park, and Ft. Collins – West. The first three of these sites are located west or south of Denver (see **Figure 1**); however, Ft. Collins is ~50 miles far north of the Denver metropolitan area and is less likely to be impacted by urban Denver emissions. The Greeley site, located in the Wattenberg oil and gas field in much closer proximity to Ft. Collins than Denver or Boulder, has a 3-year average value that is above the new 70 ppb NAAQS limit. This shows that the O_3 levels across the Front Range are elevated in a variety of geographic settings and are likely impacted by several emissions sources – not just Denver urban emissions. The spatial differences between monitoring sites are demonstrated in Supplemental Material Figure S4 for the week of July 22 to July 28, 2014. Some dates, such as the 28th, have multiple sites above the 75 ppb threshold, whereas on the 27th, only the Platteville NOAA station reached mixing ratios above 75 ppb. High O_3 production is sometimes relatively homogeneous throughout the region and sometimes influenced more locally by precursor emissions reaching a particular monitoring site.

Case studies

A detailed analysis of O_3 and a variety of other gaseous species was performed on measurements taken during three selected days of the FRAPPE/DISCOVER-AQ study period. The gases that were measured continuously on the mobile laboratory platform included O_3, carbon dioxide, CO, methane, ethane, nitrous oxide, ammonia, acetylene, and CO. Ethane and methane are co-emitted from oil and gas sources and not by biogenic methane sources. A strong correlation between them is indicative of an oil and gas source (Helmig et al., 2014). In the Northern Hemisphere, ethane is sourced predominantly from oil and gas activities and not from biofuel use or biomass burning; therefore, it is a suitable tracer for oil and gas sources (Xiao et al., 2008; Thompson et al., 2014; Helmig et al., 2016). During the sample collection phase of the study there was no significant biomass burning to contribute to the observed ethane levels. Additional oil and gas chemical tracers that were measured in flask samples are propane, benzene, n-butane, and n-pentane, each of which except for propane are co-emitted from vehicles and oil and gas activities. Oil and gas activity is the dominant source of propane in the NFR (Gilman et al., 2013; Thompson et al., 2014) and consequently many studies have utilized strong correlations of NMHCs with propane to indicate oil and gas sources of emissions (Pétron et al., 2012; Gilman et al., 2013; Swarthout et al., 2013; Thompson et al., 2014; Pétron et al., 2014; Halliday et al., 2016). Propane, benzene, n-butane, and n-pentane are not the most reactive O_3 precursors compared to more common urban VOC mixtures, but previous studies have shown they can still dominate reactivity with the OH radical when present in the large abundances measured in the Front Range (Gilman et al., 2013; Swarthout et al., 2013; Abeleira et al., 2017). Isoprene is the most prevalent naturally occurring biogenic VOC in the NFR and the average daytime mixing ratio measured at the BAO Tower during the summer of 2015 was 0.2 ppb (Abeleira et al., 2017). CO is primarily a product of incomplete combustion and

its strong association with urban pollution makes it an effective tracer of urban emission influences (Parrish, 2006; Té et al., 2012). However, there are additional regional sources of CO in the Front Range: according to emission inventory estimates, 51% of CO emissions in Weld County are emitted from highway and off-highway vehicles, 9% from fuel combustion, and 30% from petroleum and related industries (U.S. EPA, 2014). Acetylene is considered a suitable tracer of urban influence and vehicle exhaust since it is primarily emitted from automobiles (Whitby and Altwicker, 1978; Fortin et al., 2005; Pétron et al., 2012; Thompson et al., 2014). Therefore, high correlation of CO with acetylene is used in this study to identify vehicular sources for CO, while correlation with ethane implicates an oil and gas source for CO. Other chemical tracers such as ammonia, nitrous oxide, and propane along with methane are used to help attribute O_3 precursors to their respective emissions sources – agriculture, wastewater treatment plants, and oil and gas production.

NOx measurements were not made as part of the mobile laboratory suite of observations. From 2011 to 2014, statewide NOx inventory emissions decreased but absolute NOx emissions in Weld County (16% highway traffic and 7% off-highway traffic in 2014) increased by 1.8% due to increases in petroleum and related industries that accounted for 54% of NOx emissions in 2014 (U.S. EPA, 2011; U.S. EPA, 2014). NOx was measured at BAO, Platteville, and Fort Collins-West on days of the case studies. Daytime NOx values at these sites fell in the range of 2–5 ppb with somewhat higher values at the Platteville site (2–20 ppb) later into the morning (NASA, 2015). McDuffie et al. (2016) demonstrated that in this region the O_3 production efficiency is maximized for NOx mixing ratios of 1–2 ppb. The NOx observations from the fixed sites suggest that broadly through the NFR O_3 precursor NOx values fall within a regime that would sustain ample O_3 production.

Mobile laboratory data selected for this analysis were from July 23, August 3, and August 13, 2014, with the drives encompassing several regimes with varying potential for O_3 formation and particularly the impact of oil and gas related emissions. July 23 (**Figures 5–8**) captured emissions in an area minimally affected by oil and gas emissions until the end of the drive when the measurements were taken in a more central location to oil and gas activities. August 3 (**Figures 9–12**) was a high O_3 day measured by the mobile laboratory as well as at multiple stationary O_3 monitoring sites. Highly elevated ethane and methane measurements as well as decreasing CO levels implicated oil and gas operations as the major source of O_3 precursors in the drive area. August 3 also showed high levels of ammonia and nitrous oxide relative to July 23, indicating the presence of agricultural methane emissions. The drive on August 13 (**Figures 13–15**) showed high localized O_3 levels in a rural area that were not seen at the surface O_3 station in Greeley. The high O_3 was

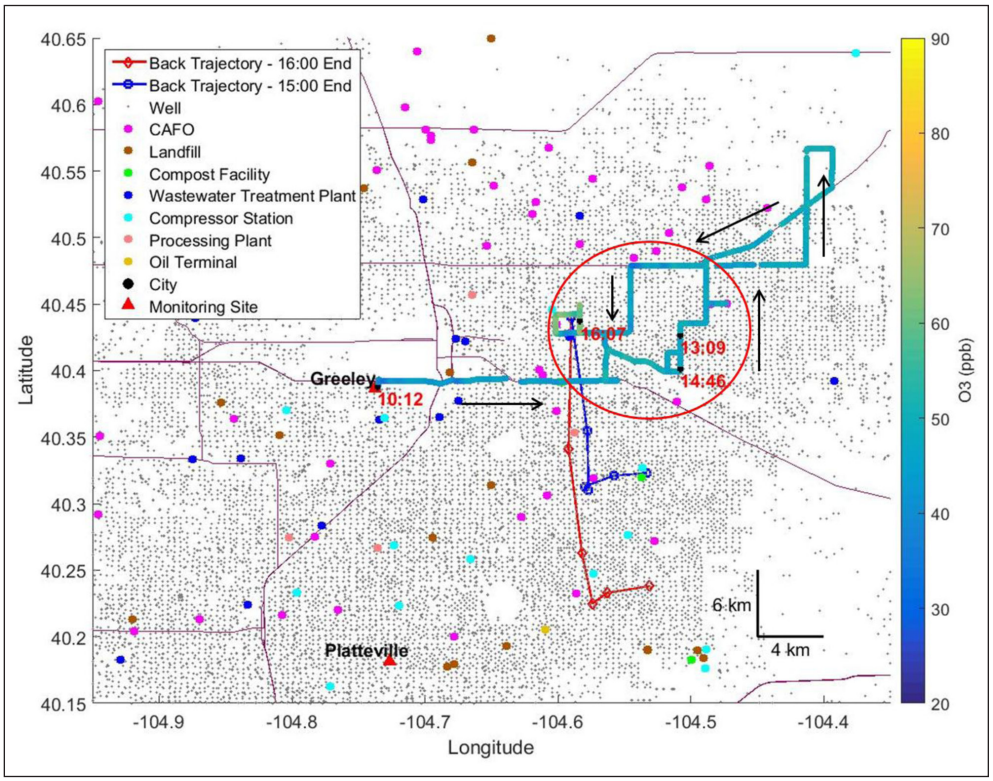

Figure 5: Map of mobile laboratory O_3 measurements on July 23, 2014. Map of O_3 measured during the mobile laboratory drive on July 23. Times in red show the location of the mobile laboratory at that time and the black arrows indicate direction of travel. Five-hour back trajectories are shown by solid lines (blue arriving at 15:00 and red at 16:00) with hourly locations noted by outlined symbols. The portion of the drive circled in red was included in Figure 6 (note that two loops were completed within the circled area at the conclusion of the drive; O_3 measurements shown were measured on the second loop). DOI: https://doi.org/10.1525/elementa.254.f5

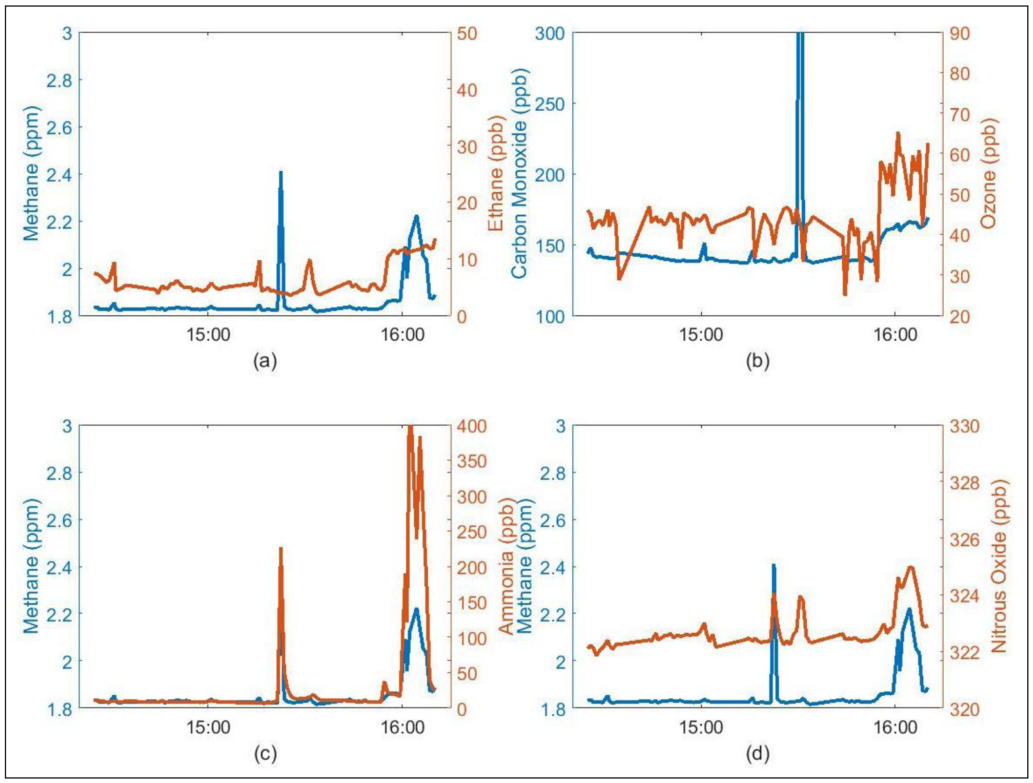

Figure 6: Time series of gaseous species from mobile laboratory on July 23, 2014. Time series plots of gaseous species measured from a mobile laboratory during period of baseline O_3 and O_3 increase on July 23. Methane and ethane **(a)**, CO and O_3 **(b)**, methane and ammonia **(c)**, and methane and nitrous oxide **(d)**. DOI: https://doi.org/10.1525/elementa.254.f6

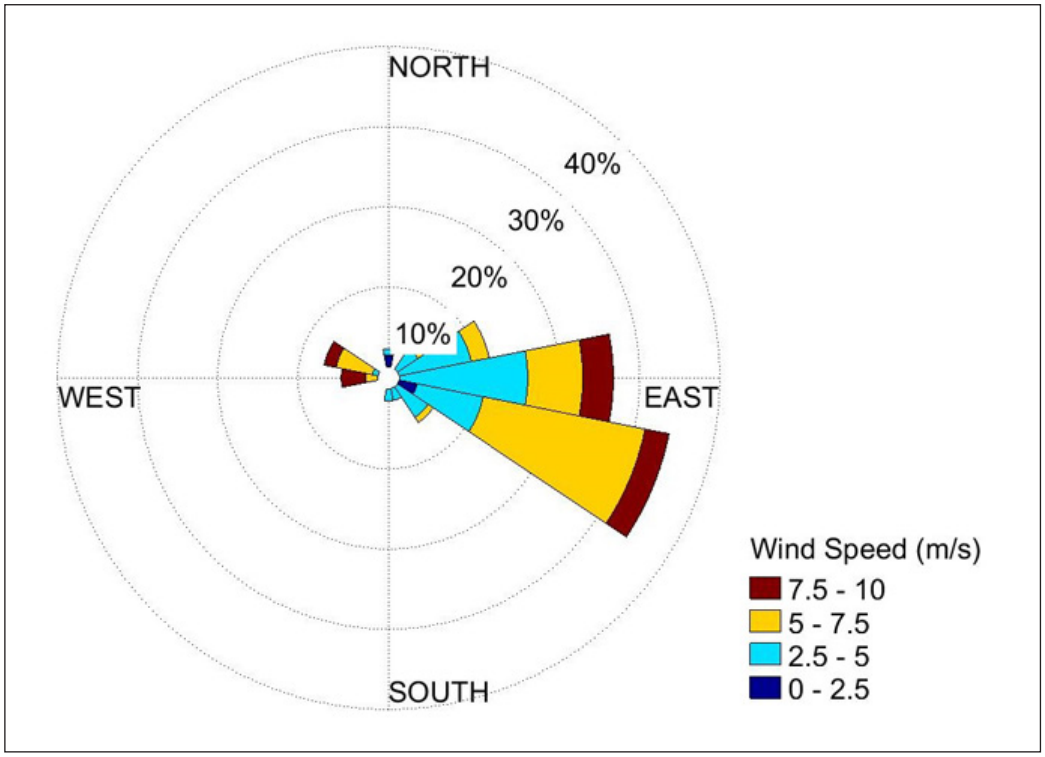

Figure 7: Wind rose from mobile laboratory drive on July 23, 2014. Wind rose displaying mobile lab meteorological data during period of baseline O_3 and O_3 increase from 14:00–16:10 on July 23. Wind speed (in m/s) is indicated by color and the percentages represent the frequency of wind coming from a particular direction. DOI: https://doi.org/10.1525/elementa.254.f7

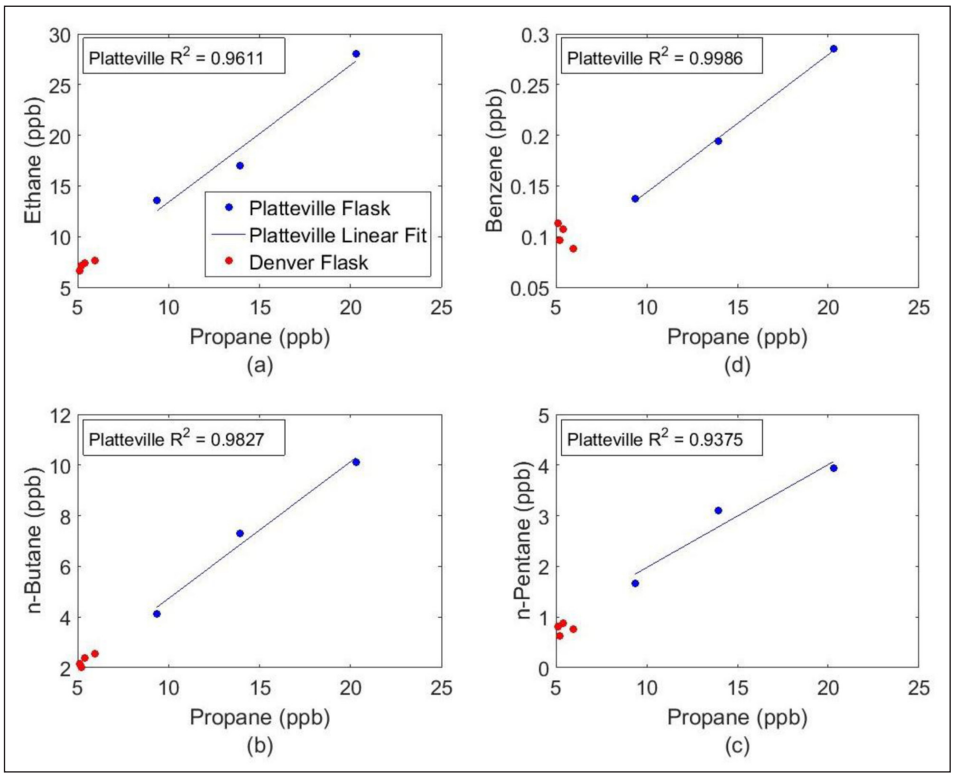

Figure 8: Mixing ratios measured in flasks collected on July 23, 2014. Mixing ratios measured in flasks collected on July 23 displaying coefficients of determination of ethane vs. propane **(a)**, benzene vs. propane **(b)**, n-butane vs. propane **(c)**, and n-pentane vs. propane **(d)**. DOI: https://doi.org/10.1525/elementa.254.f8

coincident with elevated ethane and methane and low CO levels compared to the other drives, indicating that oil and gas sources contributed significantly to the elevated O_3 mixing ratios in the area. Ethane and O_3 were not well correlated with points measured at the same time on any of the drives, but this type of instantaneous correlation was not expected since O_3 levels reflect cumulative production from precursors over a period of time as reflected in the growth rates shown in **Figure 3**. Overall, concurrent enhancement of ethane and O_3 throughout the drive was more indicative of oil and gas influence than point by point correlation.

July 23, 2014: Oil and gas emissons, moderate O_3 levels

The drive on July 23, shown in **Figure 5**, started in Greeley at 10:00 (MDT) and travelled east and north, ending at 16:10. The O_3 during this drive was low compared to the other drives, with the highest O_3 measured at the end of the drive. The O_3 was fairly constant around 50 ppb, with an abrupt increase to approximately 65 ppb occurring just before 16:00. Therefore, the majority of the O_3 on the drive was approximately median summertime O_3 levels on days with limited photochemical production (~45–55 ppb) with a peak of 15 ppb of enhancement. Surface O_3 levels measured at the stationary reference sites on the 23rd were elevated at the BAO Tower and at Platteville, with hourly averages peaking above 75 ppb, but were lower at the other sites (see Supplemental Material Figure S5). Sites to the south of the mobile laboratory drive had stronger O_3 enhancements on this day. As noted earlier in the discussion of the surface sites, there was a tendency for O_3 enhancements to be localized in a portion of the NFR on particular days (see Supplemental Material Figure S1).

Methane, ethane, CO, and ammonia mixing ratios during the afternoon were all lower than during the other two drive days (see **Figure 6**) aside from increases at the very end of the drive. Nitrous oxide measurements showed a few moderate spikes but were mostly not elevated relative to the other drives.

The weather at Greeley-Weld County airport on July 23 was cloudy in the morning but clear for the majority of the afternoon with no precipitation and a maximum temperature of 32°C (Weather Underground, 2015). Aside from some thin clouds, the afternoon was warm and sunny, suitable for photochemical O_3 production. Winds during the drive came mostly from the east, and from 14:00–16:00 they were from the east and east-southeast (see **Figure 7**). Just before 16:00 the winds throughout the entire drive region shifted and came from the west for the remainder of the drive period (Weather Underground, 2014). Since most of the drive was located in the farthest northeast area of the oil and gas field, the winds were coming from an area with fewer wells and fewer pollutant sources such as CAFOs, landfills, and wastewater treatment facilities. Near the end of the drive at 15:55, concurrent with the time of the wind shift, as the mobile laboratory moved into the heart of the oil and gas field, O_3 reached ~65 ppb, the highest measured values during the drive. The sudden increase in O_3 when the winds shifted shows the presence of sharp spatial gradients in O_3 in the middle of the oil and gas field. This O_3 increase corresponded to elevated

ethane amounts as well as spikes in methane, ammonia, and nitrous oxide a few minutes after the O_3 increase. The methane spike overlapped well with ammonia and nitrous oxide, indicating a potential agriculture and wastewater treatment facility source. The O_3 increase aligned more closely with the ethane increase, implicating oil and gas emissions as a significant source of the O_3 VOC precursors. The back trajectories in **Figure 5** show the modeled pathways of the air parcels that reached the drive route at 15:00 (blue solid line) and 16:00 (red solid line), both of which passed through the eastern edge of the gas field without traversing any large urban areas, confirming the mobile lab measurements that saw low urban emissions and modest oil and gas emissions until the increase at the end of the drive. The surface winds in **Figure 7** do not appear to reflect the broader air parcel transport to the drive area. Differences between the surface winds and the back trajectories are possibly related to the difference in height; the trajectories originated 300 m above the ground compared to the mobile laboratory wind measurements taken 3.2 m above the ground.

Flasks for hydrocarbon determinations were collected in Platteville and west of Denver near Golden (Latitude 39.7497, Longitude −105.1830) during the campaign. The flask data are plotted in **Figure 8**. The three flasks sampled at Platteville on July 23 had much higher mixing ratios of propane, ethane, benzene, n-butane, and n-pentane than any of the four flasks sampled at the Denver site on that same day. The high correlations of ethane, benzene, n-butane, and n-pentane with propane among the Platteville flasks exhibit the chemical signature of oil and gas emissions while the NMHCs in the Denver flasks were not highly correlated with propane. The propane levels measured in Platteville on July 23 (9.4–20.3 ppb) were very high relative to the annual average regional background level of 0.4 ppb (Thompson et al., 2014) and other cities and urban areas around the U.S., where typical daytime mixing ratios are in the range of 0.29–3.51 ppb (Baker et al., 2008). These high NMHC levels likely contributed to the 75–80 ppb peak O_3 measured at the Platteville surface monitoring station. Although the trajectories and surface winds suggest the possible transport of oil and gas emissions to the mobile laboratory measurement location, the majority of the mobile laboratory drive (prior to 16:00) located northeast of Platteville did not measure high O_3 or high O_3 precursors from either oil and gas or urban sources. At Platteville the average daytime mixing ratio of isoprene measured in the flasks on July 23 was 0.04 ppb, well below the average mixing ratio of 0.2 ppb that was observed at the BAO Tower during summer 2015 (Abeleira et al., 2017). This demonstrates that on July 23, natural sources of VOCs did not contribute a significant amount to O_3 production.

August 3, 2014: Mixed emissions, high O_3 day

Figure 9 shows the drive route on August 3, beginning at 10:15 and ending at 18:00. The O_3 measurements during this drive were cut off around 13:00 before resuming at 15:30, but there was consistent O_3 growth between 11:30 and 13:00 that reached 75–80 ppb (approximately 20–30 ppb above median mixing ratios on low photochemical production days) by the time the interruption in measurements occurred. High O_3 measurements were confirmed at stationary reference monitors (see Supplemental Material Figure S6), with peaks above 80 ppb at Greeley, FTC-CSU, and FTC-West primarily to the west of the high O_3 measured from the mobile laboratory. Overall there was a regional enhancement of O_3 on August 3 compared to July 23 levels, especially at the northern sites in the Front Range (Supplemental Material Figure S3).

Figure 10 shows that both methane and ethane levels were elevated above the values measured on the July 23 drive. The concurrent elevated ethane (25 to >35 ppb, much higher than on July 23rd) and methane is a marker for oil and gas emissions and shows that oil and gas O_3 precursor emissions influenced the entire area sampled by the mobile laboratory. CO levels were the highest observed during the case study days in the morning, but decreased throughout the afternoon to ~160 ppb (slightly higher than the July 23 drive), indicating the presence of urban emissions that were less significant during the period of higher O_3. The elevated CO levels from 11:15–12:15 were correlated with acetylene (not shown) with a coefficient of determination (R^2) of 0.97, indicating an automobile source. From 12:15–13:00, the modestly elevated CO values during the higher O_3 observations showed an oil and gas signature based on the correlation with ethane (R^2 = 0.81) but not with acetylene. The ammonia and nitrous oxide values were higher than on July 23, implicating an agricultural methane source, but the elevated ethane during the drive confirms oil and gas as an additional source for the methane. Overall, the gas measurements display characteristics of oil and gas and agricultural sources with some additional urban source signatures. Therefore, the O_3 production measured on the August 3 drive was likely due to a combination of local oil and gas sources as well as the transport of O_3 or precursors from urban areas since agricultural methane sources are not a significant source of NMHCs.

There was no precipitation measured at the Greeley airport on August 3 and the maximum temperature was 31°C. The sky was clear the entire day, and overall the weather was conducive to photochemical O_3 production. During the time period of increasing O_3 (11:15–13:00) the winds were mixed between the southwest, southeast, and west–northwest and the wind speeds were lower than those measured on July 23 (see the wind rose in **Figure 11**). Surface winds in the Greeley area during the early afternoon on August 3 were similar to **Figure 11** and came mostly from the south and southeast (Weather Underground, 2014). The back trajectories (see **Figure 9**) demonstrated potential transport from urban Greeley of the air parcel arriving to the drive area at 12:00 (blue solid line), while the 13:00 trajectory (red solid line) was more stagnant and originated just southwest of the high O_3 drive measurements. Back trajectories on August 3 are in basic agreement with the surface winds measured by the mobile laboratory and displayed in **Figure 11**. Based on the surface winds and back trajectories, emissions

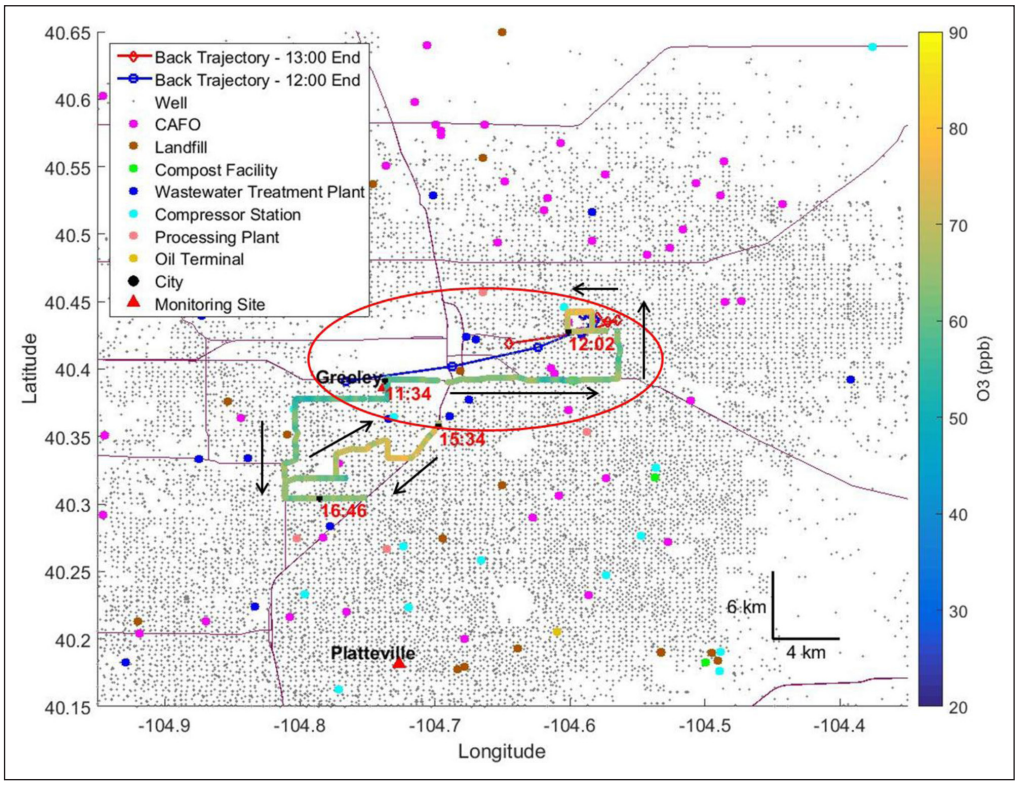

Figure 9: Map of mobile laboratory O_3 measurements on August 3, 2014. Map of O_3 measured during the mobile laboratory drive on August 3. Times in red show the location of the mobile laboratory at that time and the black arrows indicate direction of travel. Five-hour back trajectories are shown by solid lines (blue arriving at 12:00 and red at 13:00) with hourly locations noted by outlined symbols. The portion of the drive circled in red was included in Figure 10. The southern portion of the drive took place after the gap in measurements. DOI: https://doi.org/10.1525/elementa.254.f9

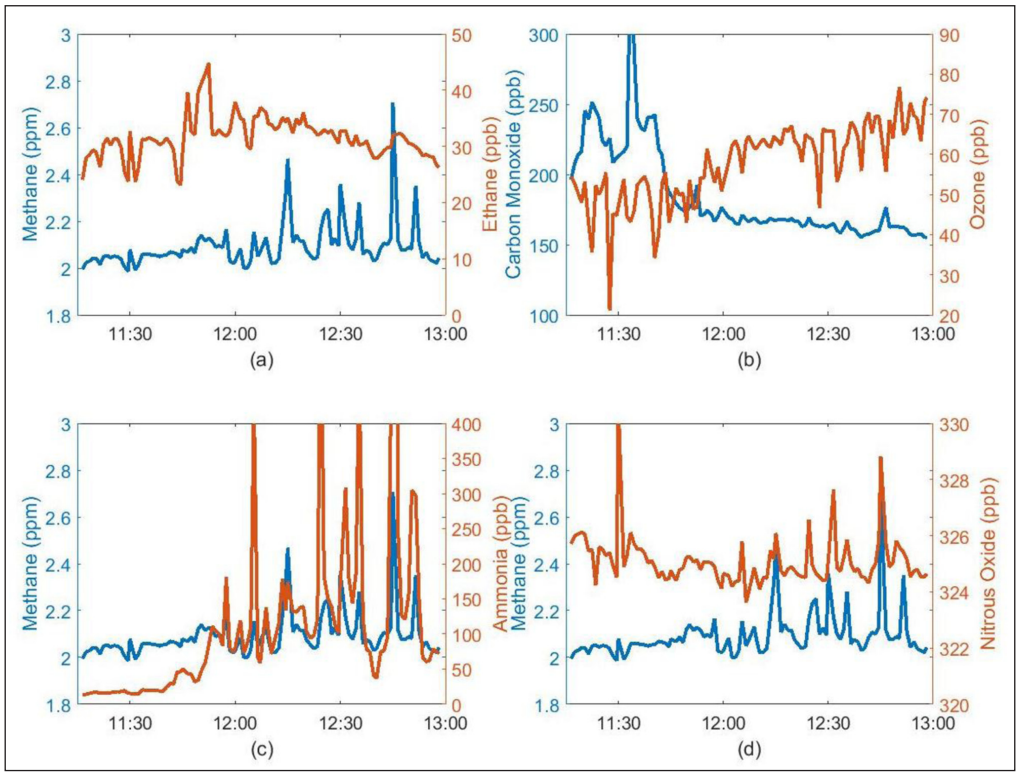

Figure 10: Time series of gaseous species from mobile laboratory on August 3, 2014. Time series plots of gaseous species measured from a mobile laboratory during period of high O_3 on August 3. Methane and ethane **(a)**, CO and O_3 **(b)**, methane and ammonia **(c)**, and methane and nitrous oxide **(d)**. DOI: https://doi.org/10.1525/elementa.254.f10

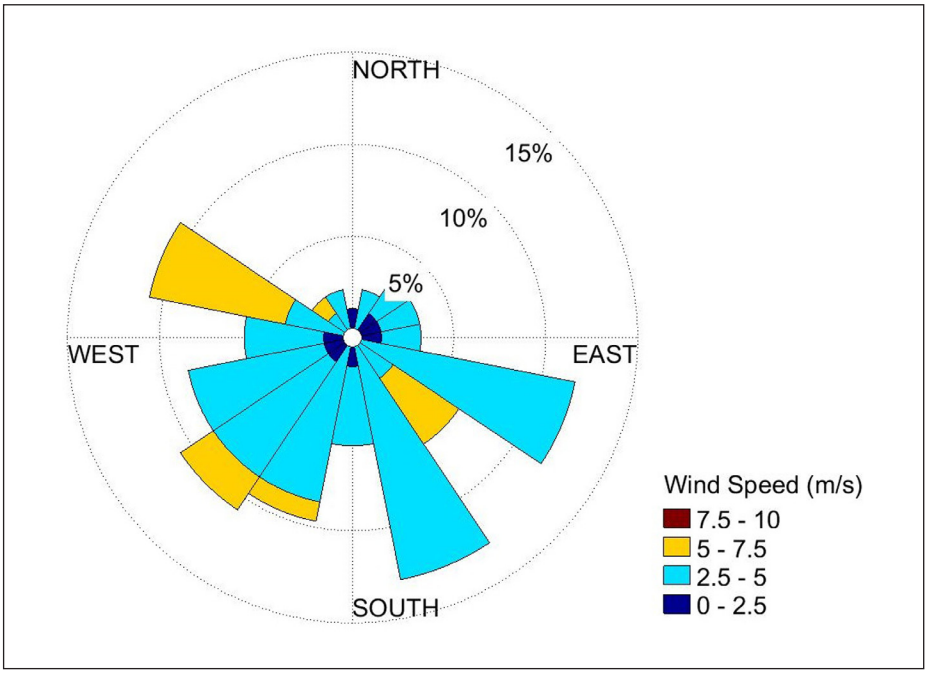

Figure 11: Wind rose from mobile laboratory drive on August 3, 2014. Wind rose displaying mobile lab meteorological data during period of high O_3 from 11:15–13:00 on August 3. Wind speed (in m/s) is indicated by color and the percentages represent the frequency of wind coming from a particular direction. DOI: https://doi.org/10.1525/elementa.254.f11

measured throughout the drive included oil and gas and agricultural sources, in addition to urban emissions plumes from the Greeley area during the earlier portion of the drive.

The flasks on August 3 (see **Figure 12**) were collected in Platteville, northwest of Denver (same site as July 23), and in the Rocky Mountains at two different sites (39.94, −105.58 and 40.38, −105.63). The Platteville flasks had significantly higher propane, ethane, benzene, n-butane, and n-pentane than any of the other flasks and they also demonstrated correlations that indicate that the source of the VOCs was oil and gas activities. The correlation coefficients on August 3 were similar to July 23, but overall the mixing ratios measured in the flasks were higher for all species on August 3 than on July 23. The flasks collected in Denver and in the Rocky Mountains all have lower light alkanes mixing ratios than in Platteville, and they also appear to be very similar to each other. This further enforces the pattern that the Platteville air was strongly influenced by local oil and gas operations emissions and those VOC emissions are not transported from Denver or the mountains to the west. The flask collected in the morning (at 8:30) had the highest oil and gas marker levels (upper right point in the plots in **Figure 12**), while the lowest levels at Platteville were measured in the afternoon at 14:30. The timing of the flask collection presents an explanation for why the surface O_3 was not as high in Platteville (peak of 67 ppb) as it was in Greeley, FTC-CSU, or FTC-West (peaks of 84, 83, and 81 ppb, respectively), despite the presence of oil and gas emissions as presented in **Figure 12**. Oil and gas O_3 precursor mixing ratios were decreasing in the Platteville area throughout the early afternoon (boundary layer growth), leading to lower peak O_3 mixing ratios measured at that surface monitoring station. On August 3 isoprene mixing ratios in the flasks at Platteville were on average only 0.03 ppb, indicating limited potential for isoprene to dominate VOC reactivity and O_3 formation.

August 13, 2014: Oil and gas emissions and localized elevated O_3

On August 13 the drive lasted from 7:20 to 14:20 and was located northeast of Greeley (see **Figure 13**). The O_3 measured during this drive was elevated ~20–30 ppb above median levels on limited production days and was approximately 75–80 ppb from 13:00–13:45. Of the surface sites, only Fort Collins–CSU recorded hourly O_3 above 75 ppb (with a peak nearing 90 ppb). Platteville and Greeley both had moderate peaks of 70 ppb (Supplemental Material Figure S4), demonstrating that the high O_3 measured on the drive was more localized to the northeast area and high O_3 at the fixed monitoring sites was most prominent at the northernmost locations (Fort Collins).

As shown in **Figure 14**, the ethane levels recorded during the high O_3 period were comparable to the measurements on the August 3, 2014 drive and remained between 30 and 40 ppb except for one dip around 13:45. These ethane levels are very high relative to the 1.29 ppb annual average regional background reported by Thompson et al. (2014). The methane level was also elevated above background levels, ranging from 2 to 2.2 ppb. The CO levels of ~150 ppb were well correlated with the ethane levels from 13:00–14:10 with a coefficient of determination (R^2) of 0.87. CO did not show correlation with acetylene for the majority of the drive until a slight increase in CO was associated with acetylene (R^2 = 0.93 from 13:55–14:10), suggesting that the dominant CO source through most of the drive was related to oil and gas

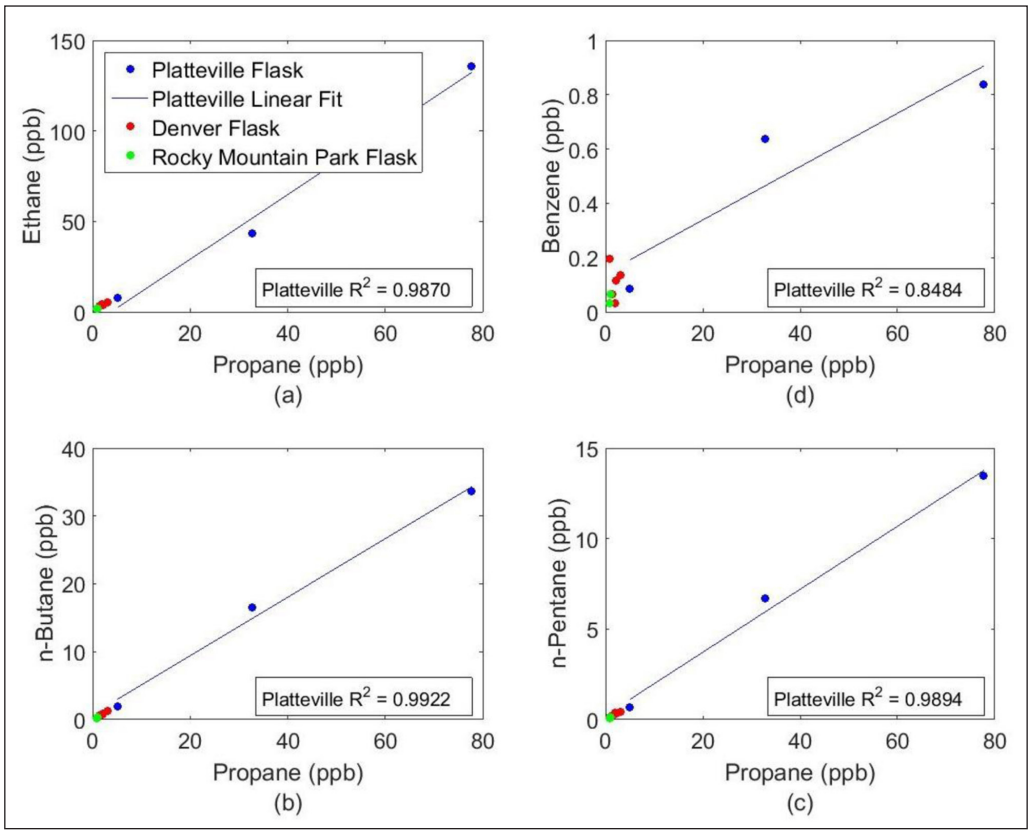

Figure 12: Mixing ratios measured in flasks collected on August 3, 2014. Mixing ratios measured in flasks collected on August 3 displaying coefficients of determination of ethane vs. propane **(a)**, benzene vs. propane **(b)**, n-butane vs. propane **(c)**, and n-pentane vs. propane **(d)**. DOI: https://doi.org/10.1525/elementa.254.f12

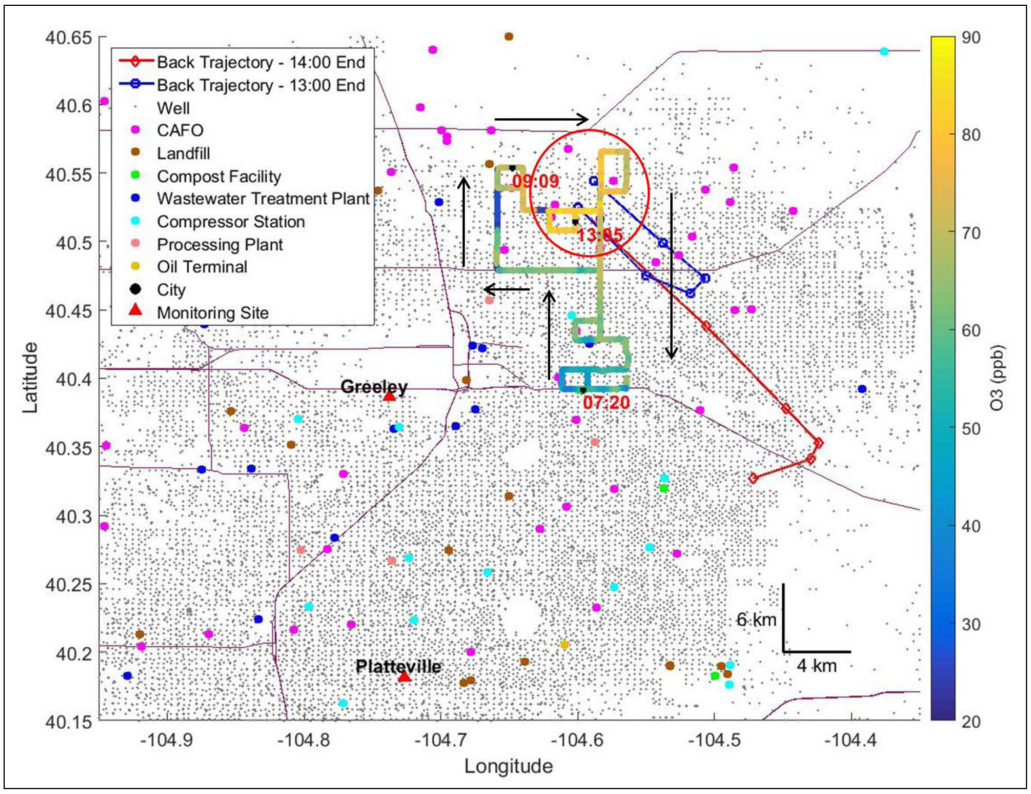

Figure 13: Map of mobile laboratory O_3 measurements on August 13, 2014. Map of O_3 measured during the mobile laboratory drive on August 13. Times in red show the location of the mobile laboratory at that time and the black arrows indicate direction of travel. Five-hour back trajectories are shown by solid lines (blue arriving at 13:00 and red at 14:00) with hourly locations noted by outlined symbols. The portion of the drive circled in red was included in Figure 14. DOI: https://doi.org/10.1525/elementa.254.f13

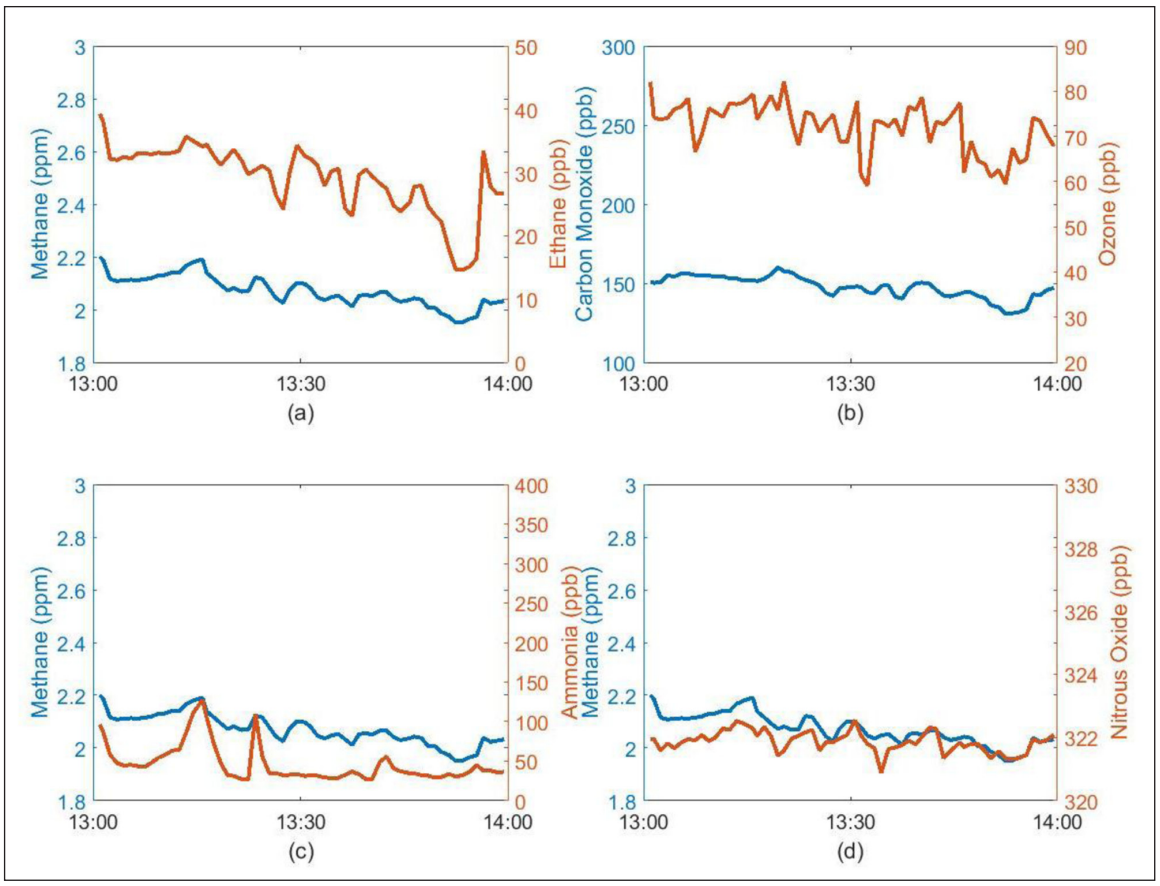

Figure 14: Time series of gaseous species from mobile laboratory on August 13, 2014. Time series plots of gaseous species measured from a mobile laboratory during period of high O_3 on August 13. Methane and ethane **(a)**, CO and O_3 **(b)**, methane and ammonia **(c)**, and methane and nitrous oxide **(d)**. DOI: https://doi.org/10.1525/elementa.254.f14

extraction and processing activity as opposed to automobiles. CO and NOx are often co-emitted from inefficient combustion processes. Oil and gas related combustion activities that likely produced the measured enhanced CO would also produce adequate NOx for O_3 production. Ammonia and nitrous oxide levels were on average much lower and did not show any of the large spikes seen on the August 3 drive, eliminating agricultural emissions as contributors to the observed methane levels.

The weather on August 13 was clear skies all day with no precipitation and a maximum temperature of 32.8°C. These conditions were similar to August 3 and favorable for O_3 generation. The wind direction during the high O_3 period on August 13 was variable, primarily out of the south, with low speed (see **Figure 15**). These winds were consistent with those measured at other sites throughout the Front Range; Platteville and BAO demonstrated predominantly southeast winds during the early afternoon and weather stations in Greeley and northeast of the drive location measured winds from the southwest and southeast from 10:00 AM to 1:00 PM (Weather Underground, 2014). These sites confirm that winds on August 13 did have significant southerly components that could carry O_3 precursors to the northern portion of the gas field where the drive took place. Back trajectories shown in **Figure 13** (blue and red solid lines) confirmed that air parcels reaching the drive route during the period of high O_3 originated in a remote area of the gas field with oil and gas emission sources (wells) and agricultural sources (CAFOs), but did not pass through more urban areas. Although the winds are generally light, the dominant direction out of the south is consistent with the air parcel transport shown in the trajectories. The surface winds and trajectories, coupled with the low levels of ammonia and nitrous oxide measured during the drive, indicate that no O_3 precursor emissions other than oil and gas related were observed.

The flasks from August 13 were all located slightly north of Denver with the exception of one flask in Platteville. The Platteville flask had moderate mixing ratios of oil and gas tracers and an isoprene mixing ratio of 0.06 ppb. Overall, the flask data did not provide significant additional insight into pollution sources during the drive, but they did show that isoprene mixing ratios were not significantly higher on August 13 than on July 23 or August 3, demonstrating that isoprene was not likely to be the major source of VOCs for the high O_3 measured during the drive.

The average mixing ratios of ethane, CO, and O_3 that were measured by the mobile laboratory on the three case study drives are shown in **Figure 16**. While on July 23 and August 13 the O_3 had likely reached the daily peak by the drive times shown in **Figure 16** (See Supplemental Material Figure S5 and Figure S7 – typically O_3 reaches the daily peak by ~14:00), based on measurements at the

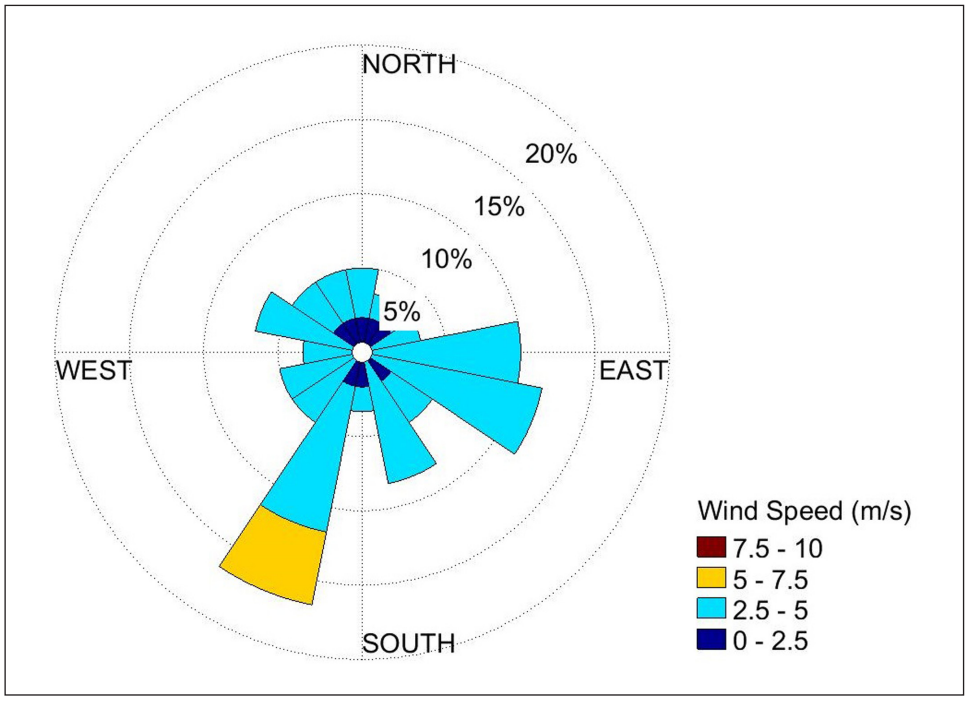

Figure 15: Wind rose from mobile laboratory drive on August 13, 2014. Wind rose displaying mobile lab meteorological data during period of high O_3 from 13:00–14:00 on August 13. Wind speed (in m/s) is indicated by color and the percentages represent the frequency of wind coming from a particular direction. DOI: https://doi.org/10.1525/elementa.254.f15

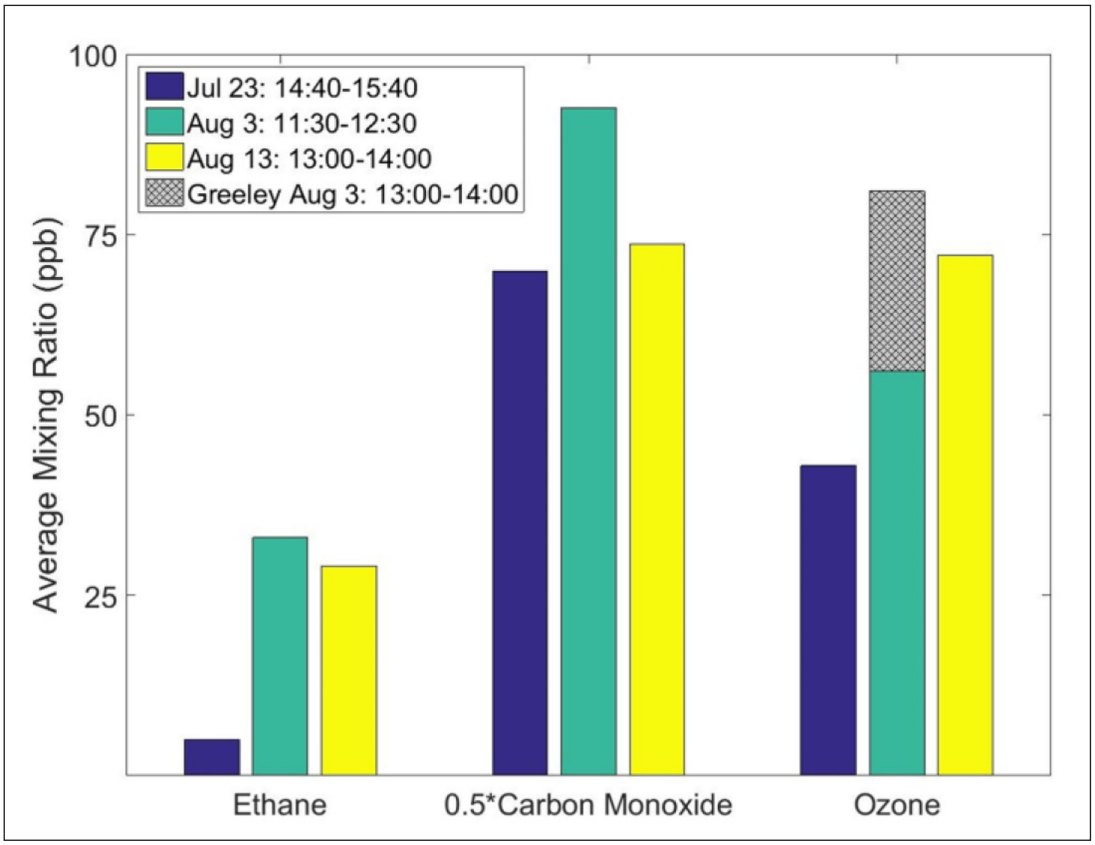

Figure 16: Average ethane, CO, and O_3 measured during the case study drives. Averages of one hour of measurements of ethane, CO, and O_3 during the mobile laboratory drives on July 23, August 3, and August 13, 2014. The time of day of each drive that was included is shown in the legend. Average O_3 at the Greeley monitoring site from 13:00–14:00 is included (gray cross hatched square) to estimate peak O_3 in the drive vicinity on August 3. DOI: https://doi.org/10.1525/elementa.254.f16

nearby Greeley monitoring site, on August 3 it is likely that additional growth would have taken place in the vicinity of the mobile laboratory drive. The average O_3 at Greeley from 13:00–14:00 was 81 ppb and that value is included in **Figure 16** as an estimate for the peak value along the drive route. August 3 and 13 demonstrated higher average O_3 and ethane than July 23 as measured by the mobile laboratory. August 3 showed more potential for urban emission influence on O_3 production with the highest average CO levels of the three days, but the highly elevated ethane on August 3 shows definite presence of oil and gas O_3 precursors on that day. August 13 demonstrates that in the NFR, high O_3 can be produced in portions of the basin on a day when the dominant emission signature is oil and gas (indicated by ethane levels well above regional background) with low urban emissions (indicated by CO). The high O_3 mixing ratios measured by the mobile laboratory on August 13 were not observed at the Greeley and Platteville surface monitors and the surface winds did not implicate transport of O_3 from other areas as the source of the high O_3. These findings demonstrate that oil and gas activities were the primary source of O_3 production of 20–30 ppb above median summertime levels observed northeast of Greeley on the drive on August 13, 2014.

Conclusions

Median summertime NFR O_3 mixing ratio on days with limited photochemical production within the boundary layer was within the range of 45–55 ppb based on observations at Pawnee Buttes, a monitoring site that is minimally impacted by Front Range emissions. During the summer of 2014, O_3 levels were lower on average than the summer of 2013, but there were still exceedances of the EPA NAAQS standard of 75 ppb (8-hour average) at multiple sites throughout the Front Range.

Three case study days were selected from the FRAPPE/DISCOVER-AQ study period to evaluate O_3, emissions linked to O_3 precursors, and meteorology, using extensive measurements collected throughout the Front Range by instrumented vehicles. These case studies form the basis for attributing oil and gas related emissions to significant O_3 enhancements seen on two of the drives while the third drive provides a baseline case with relatively low O_3 enhancement and lower emissions with potential for O_3 formation. Three dates of interest considered in this study were July 23, August 3, and August 13, 2014. The weather during these three afternoons was consistently sunny and warm and therefore conducive to photochemical O_3 production.

July 23 represented a lower, background-level emissions day for the Greeley region where the mobile laboratory drive took place, with low mixing ratios of ethane, methane, CO, ammonia, and nitrous oxide relative to other days. O_3 measurements on the drive were equal to median levels on low photochemical production days (~45–55 ppb), with a spike of 15 ppb of O_3 enhancement as the mobile laboratory moved closer to the heart of oil and gas emissions. High O_3 levels were measured at the Platteville monitoring site, as were high oil and gas NMHCs. O_3 levels on August 3 were high at multiple monitoring stations, and the mobile laboratory drive measured O_3 up to 30 ppb above median low photochemical production summertime levels concurrently with elevated ethane and methane, indicating the presence of oil and gas emissions. Based on back trajectories and correlations of CO with acetylene and ethane, the high O_3 observed on August 3 was due primarily to oil and gas emissions with additional urban influence. The mobile laboratory drive on August 13 provided a strong case for examining the potential impact of oil and gas emissions and related activities on O_3 production in the NFR of Colorado. The drive on August 13 measured high O_3 levels (20–30 ppb above median low photochemical O_3 production days) in a remote area northeast of Greeley. High O_3 levels were linked to elevated ethane and methane, similar to the August 3 case, indicating an oil and gas source of O_3 precursors but with low mixing ratios of tracers of agricultural and urban emissions. Although wind data from the mobile laboratory platform suggested possible transport from both oil and gas and urban areas to the remote drive area on this day there was a clear absence of any measured urban pollution signature confirmed by the back trajectory analysis. While previous studies have focused on the overall enhancement of O_3 due to oil and gas in the Front Range and found the impact to be between 6 and 11 ppb, these results demonstrate that on individual days, oil and gas can contribute locally up to 30 ppb to O_3 production.

The complex meteorology of the NFR in combination with the variety of emission sources, create a unique setting for high summertime O_3 levels. The data presented in this paper indicate that high O_3 is occurring in remote areas in the Wattenberg oil and gas field on days when oil and gas related emissions are the dominant source of precursors. Based on this work, more extensive measurements of O_3, NOx, and NHMCs in the NFR are recommended to better understand spatial variability in O_3 formation and quantify the magnitude of the contributions from each emission sector throughout the region. Better understanding of emissions and of the relative contributions of the various pollutants in the region will increase the effectiveness of mitigation actions and regulations. Since exceedances of EPA standards are based on single days and not overall enhancement averaged over multiple days, the high O_3 mixing ratios measured on days when oil and gas activity is a primary contributor to elevated O_3 levels make it imperative to better quantify O_3 production contribution from oil and gas operations emissions to support strategies for staying within the NAAQS for O_3 in the region.

Data Accessibility Statement

Data sources are cited in the text of the manuscript with the URLs listed in the references.

Supplemental Files

The supplemental files for this article can be found as follows:

- **Figure S1.** Comparison of mobile laboratory O_3 measurements with Greeley monitoring site on August 8, 2014. DOI: https://doi.org/10.1525/elementa.254.s1

- **Figure S2.** Comparison of mobile laboratory O_3 measurements with Greeley monitoring site on August 3, 2014. DOI: https://doi.org/10.1525/elementa.254.s1
- **Figure S3.** Comparison of mobile laboratory O_3 measurements with Greeley monitoring site on August 5, 2014. DOI: https://doi.org/10.1525/elementa.254.s1
- **Figure S4.** O_3 measurements at six surface sites for a week in July 2014. DOI: https://doi.org/10.1525/elementa.254.s1
- **Figure S5.** O_3 measurements at six surface sites on July 23, 2014. DOI: https://doi.org/10.1525/elementa.254.s1
- **Figure S6.** O_3 measurements at six surface sites on August 3, 2014. DOI: https://doi.org/10.1525/elementa.254.s1
- **Figure S7.** O_3 measurements at six surface sites on August 13, 2014. DOI: https://doi.org/10.1525/elementa.254.s1

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Competing interests

The authors have no competing interests to declare.

Author Contributions

- Contributed to conception and design: LCC, SJO, GP
- Contributed to acquisition of data: EJM, SCH, DB, AMT, AM-B
- Contributed to analysis and interpretation of data: LCC, SJO, GP, RCS, EJM, DRB, AMT
- Drafted and/or revised the article: LCC, SJO, GP, RCS
- Approved the submitted version for publication: LCC, SJO, GP, RCS, EJM, SCH, DRB, AMT, AM-B

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